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(54) Title: METHOD FOR FORMING A LUBRICATIVE FILM FOR COLD WORKING		
(57) Abstract		
<p>A phosphate conversion coating of 6 to 20 g/m² is formed on a metal substrate, using an electrolytic solution containing zinc ions, phosphate ions, and an auxiliary acid, preferably nitric acid, and passing an electric current, with the substrate serving as the cathode, for a few seconds through the substrate, the electrolyte solution, and a counterelectrode. This provides a method for forming a lubricative film suitable for cold working without generating any sludge and at a high level of productivity. Lubrication performance may be checked by means of a backward punching test. The dies (2) are set to bind the circumference of the cylindrical test specimen (1) and the specimen is then subjected to a downward stroke from a punch (3).</p>		

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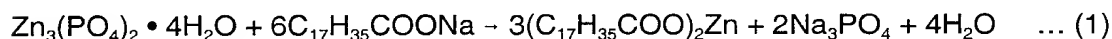
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Description**METHOD FOR FORMING A LUBRICATIVE FILM FOR COLD WORKING****BACKGROUND OF THE INVENTION**

The present invention relates to a method for forming a lubricative film for the cold working of metal materials, which is used for the purpose of reducing the friction that occurs between a tool and a work piece, thereby preventing seizure during the cold working of metal.

A method widely employed in the past in the field of the cold plastic working of metal materials involved forming a chemical conversion film as a lubrication undercoating on the surface of a metal material, and forming a lubricative film over this by a lubrication treatment featuring a water- or oil-based lubricant. For example: a phosphate treatment using zinc phosphate, zinc-iron phosphate, zinc-calcium phosphate, manganese phosphate, iron phosphate, or the like has been performed on carbon steel or low-alloy steel; an oxalate treatment has been performed on stainless steel; a chemical conversion film treatment in which the main component of the film is an aluminum fluoride has been performed on aluminum; a chemical conversion film treatment in which the main component is copper oxide has been performed on copper; and a conversion film treatment in which the main component is titanium fluoride has been performed on titanium. (*Process Tribology*, edited by the Japanese Plastic Working Society, pp. 56 - 62 (Corona, 1993)).

After the formation of a chemical conversion film, the general practice is to form a lubricative film using a water- or oil-based lubricant. In particular, when a phosphate treated material is brought into contact with a weakly alkaline aqueous solution of a fatty acid alkali metal salt, a lubricative film with a three-layer structure composed of a phosphate film, a metal soap, and a soap (this three layer structure being hereinafter referred to as a reaction type soap film) is formed on the material surface, and this method is called a reaction type soap treatment. The reaction is expressed by the following chemical equation (1):



Reaction type soap films are the most commonly used lubricative films because they provide good lubrication performance even under harsh cold forging conditions. The process steps or operations generally entailed by a reaction type soap treatment are as follows:

1. Descaling (acid pickling with sulfuric acid, hydrochloric acid, or the like, or mechanical descaling by shot blasting or the like combined with acid pickling with

- sulfuric acid, hydrochloric acid, or the like);
2. Rinsing with water;
 3. Chemical conversion film treatment;
 4. Rinsing with water;
 5. Reaction type soap treatment;
 6. Drying.

Nevertheless, the lubricative film formation methods used in the past had several drawbacks in terms of performance and their environmental impact. These are described below.

10 The first problem is the generation of sludge. For example, in the phosphate treatment of an iron-based material, the ferrous ions that are dissolved into the treatment liquid by etching are turned into ferric ions through the action of an oxidation promoter, and this product is generally removed from the system as iron phosphate sludge, which is the source of the above-mentioned sludge generation. Similarly, large amounts of
15 sludge are generated in oxalate treatments, fluoride treatments, and oxide treatments, and people involved in the field of industrial waste are currently dealing with the disposal of this sludge.

Sludge management is disclosed in Japanese Laid-Open Patent Application 2-197581, for example, which deals with a method for reducing the amount of sludge by
20 lowering the treatment temperature by using a treatment liquid to which a water-soluble aromatic compound having nitro groups and sulfone groups has been added. While this is indeed an effective method, the reduction in sludge generation is still only about half that in the past, and further reductions are needed.

A second problem is waste liquid treatment. Over time, the liquids used in the
25 oxalate treatment of stainless steel or in the chemical conversion treatment of aluminum, copper, or titanium lose their strength, so that the resulting film no longer performs the same as it did at first, and therefore the treatment liquid has to be discarded and replaced every so often. This waste liquid is processed with wastewater equipment, or, for production lines not having such equipment, industrial waste treatment specialists
30 take over. Because the waste liquids contain various substances, including the components contained in the treated metal materials and the liquid components from pre-treatments such as degreasing and acid pickling, this wastewater treatment is tremendously expensive. Furthermore, as of now no practical way to regenerate these liquids has been implemented.

35 A third problem is that the lubrication undercoating that can be formed is limited by the material intended for chemical conversion treatment. For example, because the

above-mentioned reaction type soap film is not formed on a copper oxide film or a titanium fluoride film, a lubricative film is formed by coating the surface of the material in question with a metallic soap or an oil-based lubricant whose lubricity has been enhanced by the addition of an extreme-pressure additive. However, the performance of these lubricants is inherently inferior to that of reaction type soap films, and the cross-section reduction ratio per drawing pass cannot be increased in plastic working, so this inevitably requires more working passes, including the lubricative film treatment step. The result is a higher production cost.

Conversely, with an oxalate film or an aluminum fluoride film, the reactive soap tends to react excessively, and changes in the treatment time or liquid temperature cause undesirable and large changes in the amount of metallic soap generated. Friction increases if a smaller amount of metallic soap is generated, but on the other hand, if the metallic soap is generated excessively, beyond the proper amount, then it will tend to clog the tool. Moreover, excessive reactivity leads to a need to replace the reactive soap treatment liquid more often. Working is sometimes performed using a lubricative film formed by a lubricant whose principal component is molybdenum disulfide and using an oxalate film as a lubrication undercoating in the hot forging of stainless steel, but a problem with this method is that the iron oxalate that is the main component of the oxalate film decomposes in the course of the preheating of the material. These problems occur because the chemical conversion treatment is material-selective, and there is a need for a lubricative film formation method that is unrelated to the type of metal material being used, and which therefore does not have these problems.

A fourth problem is that it is difficult to produce the amount of lubricative film required by a chemical conversion treatment. Specifically, when a chemical conversion film is used as a lubrication undercoating, the formation of the chemical conversion film proceeds through the corrosion of the metal, so that a passivation layer is produced, which covers the metal surface and stops the production of the film. In view of this, the concentration of the chemical conversion treatment liquid, the treatment temperature, the acid ratio, and other conditions are generally set with an eye toward controlling the amount of film. With these methods, however, precise control of the film amount can not be achieved just by setting general treatment conditions, and if an attempt is made to set the treatment conditions for every metal material to be treated, there will be a marked drop in production efficiency. In view of this, the actual practice is for the working conditions to be set up for the material that is the most difficult to work, which is done as a safety factor in real production.

Another method for forming a phosphate film is an electrolysis treatment that

makes use of an external power source. Japanese Laid-Open Patent Application 6-322592, for example, discloses a method in which a phosphate film is formed by a pulse current using a steel material as the anode, after which a sodium stearate treatment is performed to produce a reaction type soap film. This method, however, generates sludge because the phosphate film production proceeds while the steel material is dissolved.

The present invention is a method for forming a lubricative film for cold working on a metal material, and an object thereof is to provide a novel method for forming a lubricative film with which at least some, and most preferably all, of the above-mentioned problems encountered in the past can be solved.

BRIEF SUMMARY OF THE INVENTION

The inventors have learned that it is desirable for the chemical conversion film to have a thickness corresponding to a mass per unit area of 6 to 20 grams of film per square meter of surface coated, this unit of areal density or "coating weight" as it is usually called being hereinafter usually abbreviated as "g/m²". With conventional methods, more sludge was produced if such a thick chemical conversion film was formed. A subordinate object of the present invention is accordingly to form a thick phosphate conversion film without producing so much sludge. Also, with conventional methods, a long contact time with the chemical conversion treatment liquid was required to form a thick conversion film; this diminished productivity. An additional subordinate object of the present invention is to form a thick phosphate conversion film at a high level of productivity. Further, with conventional methods, it was not easy to form a thick phosphate conversion film on stainless steel or the like, for example. A third subordinate object of the present invention accordingly is to provide a method with which a thick phosphate conversion film can be formed even on stainless steel or the like.

One major embodiment of the present invention is a process for forming a lubricative film for cold working, said process comprising the following operations:

- (I) bringing said metal substrate into contact with an aqueous electrolyte solution comprising, preferably consisting essentially of, or more preferably consisting of water and:
 - (A) dissolved zinc cations;
 - (B) dissolved phosphate anions; and
 - (C) at least one dissolved auxiliary acid other than phosphoric acid, said auxiliary acid having at least a first ionization constant that is greater than the third ionization constant for phosphoric acid; and, optionally, other constituents as detailed further below,

this aqueous electrolyte also being in contact with a counter-electrode that is not said metal substrate to be cold worked, so that an electric current can pass through the counter-electrode as anode, the aqueous electrolyte solution by ionic conduction, and said metal substrate as cathode;

- 5 (II) passing through said metal substrate while it remains in contact with said aqueous electrolyte solution an electric current that has a net cathodizing character at said metal substrate for a sufficient time to form an adherent solid phosphate conversion coating over said metal substrate;
- (III) discontinuing contact between said aqueous electrolyte solution and said metal
10 substrate bearing said adherent solid phosphate conversion coating; and
- (IV) applying to the exterior surface of said solid phosphate conversion coating, when it is not in contact with said aqueous electrolyte solution, a water- or oil-based lubricant coating.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Figure 1 is a cross-sectional view of apparatus used in a backward punch test that was run to test the efficacy of lubricant compositions and processes according to the present invention. Figures 2a through 2d are projection views of test substrates used in this test before being tested, while Figures 3a through 3d are projection views of the same test substrates after being punched.

20 DETAILED DESCRIPTION OF THE INVENTION AND ITS PREFERRED EMBODIMENTS

Metal substrate materials that can be used in the present invention include any electrically conductive materials, including ferrous materials such as carbon steel, chromium steel, chromium-molybdenum steel, nickel-chromium steel, nickel-chromium-
25 molybdenum steel, stainless steel, boron steel, and manganese steel, and non-ferrous materials such as aluminum, magnesium, titanium, and copper.

Preferably, a process according to the invention is applied to a metal substrate which has, if it has been normally soiled by any working oil or other foreign matter used in some previous working operation or has any scale formed in a previous operation,
30 been cleaned and pickled before being contacted with the aqueous electrolyte solution in operation (I) of a process according to the invention as described above. A commercially available alkali-based cleaning and degreasing agent preferably is used for the initial cleaning treatment when any oil or similar lubricant has been applied to the metal surface in a previous processing operation.

35 If any visible scale remains after cleaning, mechanical descaling is often preferred as the next preparatory operation for the substrate surface eventually to be

cold worked. Mechanical descaling includes the use of a bending roll, shot blasting, air blasting, and liquid honing. After mechanical descaling, any remaining scale preferably is removed by a high-pressure water jet or brushing.

Acid pickling may alternatively be used alone or in combination with mechanical
5 descaling to remove any scale present on the surface of the metal substrate to be cold worked. Sulfuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, hexafluorozirconic acid, or the like can be used for the acid pickling liquid. The acid pickling can also include the use of electrolysis with the metal substrate as anode and/or cathode. After
10 this acid pickling, the pickled surface preferably is thoroughly rinsed with water so that the acid pickling liquid is not admixed into the surface conditioning treatment liquid and/or the phosphate treatment liquid used later. It is preferable for acid pickling to be performed after mechanical descaling, if the latter is used, and it is preferable for acid pickling to be used even on substrates with no visible scale on the surface, because the pickling facilitates the formation of a good phosphate conversion coating later.

15 In order to raise the phosphate film production rate and produce finer crystals in the phosphate film, the substrate normally preferably is brought into contact with a pre-treatment liquid containing colloidal titanium, or with a pre-treatment liquid in which a metal phosphate including particles whose diameter is 5 micrometres, hereinafter usually abbreviated as " μm ", or less has been dispersed, before beginning operation (I) of a
20 process according to the invention as described above, but after any chemical cleaning, descaling, and/or pickling as described above. It is also effective to heat the treated material immediately prior to the phosphate treatment, in which case the rate at which the phosphate film is produced will increase.

As already noted, the aqueous electrolyte solution utilized in operation (I) of a
25 process according to the invention as described above must contain dissolved zinc ions. Preferably, these ions are supplied from a source, such as a water soluble salt of zinc, in which zinc is already present in cationic form and is expected to remain in cationic form when dissolved, or from a source such as zinc metal or zinc oxide, that is expected to react with acid already present in a precursor solution made during the course of pre-
30 paring the final aqueous electrolyte solution to be used in a process according to the invention. Any zinc present in these sources that are mixed to make up the final aqueous electrolyte solution used in a process according to the invention is to be presumed for purposes of this description as present in cationic form to the full extent stoichiometrically possible from the amount of zinc contained in the source(s) used in
35 making the aqueous electrolyte solution, irrespective of any incomplete dissociation, complex formation, or the like that may occur in this electrolyte solution.

The dissolved phosphate anions required for the aqueous electrolyte solution used in operation (I) of a process according to the invention as described above may be sourced to this solution by any water soluble salts, including only partially neutralized salts, of orthophosphoric or condensed phosphoric acids and/or by these acids themselves. The full stoichiometric equivalent as PO_4^{-3} anions of all such substances mixed to make the aqueous electrolyte solution are to be understood for purposes of this description as constituting dissolved phosphate anions therein, irrespective of the actual degree of dissociation, complex formation, condensation to make polyphosphoric acids or their anions and the like that may occur in the actual electrolyte solution. At least for economy, orthophosphoric acid itself and/or its water soluble zinc salts are preferred as sources over any other substances.

The third necessary component of the aqueous electrolyte solution used in a process according to this invention as described above is an auxiliary acid. It is preferred for this auxiliary acid to have at least a first ionization constant that is at least, with increasing preference in the order given, 10^{-5} , 10^{-4} , 10^{-3} , 10^{-2} , or 0.10. Nitric acid is particularly preferred as the auxiliary acid, but any other sufficiently strong acid that does not interfere with the intended operation of a process according to the invention may also be used. Quantitative preferences will be given below in terms of nitric acid, but amounts of any other strong acid that does not produce a noxious product of anodization, precipitate any desired constituents of the electrolyte solution, cause metallic zinc instead of zinc phosphate to be coated on the cathodized substrate, or in any other manner damage or severely frustrate the process as described for nitric acid and that results in an electrolyte solution with the same pH value as those of solutions containing preferred amounts of other constituents along with the preferred amounts of nitric acid specified below can also be used in a process according to the invention.

The aqueous electrolyte solution used in a process according to the invention preferably contains, independently for each constituent stated and independently for the lower and upper limits of preferred concentrations stated:

- 20 to 50 grams of zinc ions per liter of electrolyte solution, this concentration unit of grams of a constituent per liter of any composition being hereinafter usually abbreviated as "g/l";
- 20 to 70 g/l of phosphate ions; and
- 30 to 80 g/l of nitric acid.

If the zinc ions content is less than 20 g/l, the phosphate ions content is less than 20 g/l, or the nitric acid content is less than 30 g/l, it will often take an undesirably long time to form a chemical conversion film of the desired thickness, so that productivity of the

process will be suboptimal. If the amount of nitric acid is less than 30 g/l, good coverage of the surface with a phosphate film can not normally be achieved because metallic zinc will co-deposit preferentially, so that good lubricity will not be obtained. However, it is sufficient for the zinc ions content to be no more than 50 g/l, the phosphate ions content to be no more than 70 g/l, and the nitric acid content to be no more than 80 g/l. No particular benefit in productivity will normally be obtained by raising these concentrations any higher and more of the ingredients of the phosphate treatment liquid will be wasted by dragout, so that the cost of the process will be increased without any compensating economic benefit.

In the phosphate treatment liquid, it is independently preferable for the molar ratio of metal ions to phosphate ions to be from 0.3 to 2, and for the molar ratio of nitric acid to phosphate ions to be from 0.1 to 3. If the molar ratio of metal ions to phosphate ions is less than 0.3, it will be difficult to produce a phosphate film at an economically attractive rate. If this ratio exceeds 2, a film will still be readily produced, but the electrolyte solution will be more costly without any offsetting economic benefit. If the molar ratio of nitric acid to phosphate ions is below 0.3, there is a danger that zinc plating will occur preferentially, but if this ratio exceeds 3, the crystals in the phosphate coating formed will be undesirably coarser.

It is preferable for the electrolyte solution used in operation (I) of a process according to the invention as described above to contain, in addition to zinc, at least one type of divalent or trivalent metal ions selected from among magnesium, aluminum, calcium, manganese, chromium, iron, nickel, and copper. It is especially preferable for the metal ions in the phosphate treatment to comprise, or more preferably to consist essentially of, zinc and calcium. If these ions comprise zinc and calcium, then it is preferable for the molar ratio of calcium ions to zinc ions to be between 0.1 and 2. A cathodic electrolysis treatment conducted in this treatment liquid will yield a zinc phosphate film that contains both $\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$. The higher the molar ratio of calcium to zinc, the higher will be the content of calcium zinc phosphate. Only a zinc phosphate film will be produced if the molar ratio is less than 0.1, but if 2 is exceeded, little or no calcium zinc phosphate will be produced, and instead a calcium monohydrogenphosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) coating will be produced.

The phosphate treatment is conducted using the metal substrate as the cathode. The type of electrolysis may be either direct current, sine wave, or square wave, and it is also possible to use a method in which a direct current waveform is used as a bias, and a sine wave or square wave is superposed over this. The electrolysis may be controlled by means of the current or the voltage. Counter-electrodes that can be used for

the electrolysis treatment include electrodes made of carbon, stainless steel, platinum, titanium alloy, and titanium-platinum-covered alloy.

With the present invention, because the phosphate film is formed while the substrate metal is kept cathodic, metallic components of the substrate are not eluted into the treatment liquid. Therefore, there is normally no sludge production whatsoever, nor is there necessarily any decrease in the performance of the treatment liquid, and no need whatsoever to discard and replace the treatment liquid, provided that the constituents of the electrolyte solution that are incorporated into the phosphate coating formed are replenished in the electrolyte solution. (The metal ions incorporated into the phosphate coating formed can be replenished continuously if the same type of metal as that of the metal ions contained in the treatment liquid is used for the anode, but in this case the liquid must be managed so that the amount of metal ions is kept constant in the treatment liquid. The metal ions, alternatively, and the phosphate ions incorporated into the phosphate coating formed can be replenished by addition of one or more replenishers that contain them. Any adverse change in the electrolyte solution that occurs as a result of anodic reactions at the counter-electrode can also be corrected by suitable replenishment.)

Also, in a process according to the invention, the temperature of the treatment liquid can be much lower than in the past, and treatment at normal ambient human comfort temperature is possible, so that there is a significant savings in the thermal energy entailed by the treatment. Further, because a phosphate film can be formed regardless of the type of metal substrate with the present invention, high cold working forces can be used, even on substrates with which this was difficult with conventional methods. For instance, copper or stainless steel can be subjected to a phosphoric acid treatment and then to a reaction type soap treatment.

In addition, because the amount of phosphate film can be set as desired, it is possible to obtain a lubricative film in the required amount that is suited to the cold working subsequently performed. The film amount can be controlled by means of the treatment liquid concentration, the treatment liquid temperature, the current density, and the treatment duration.

The higher the treatment liquid concentration, the greater is the possible phosphate film amount, but a concentration that is too high will be economically disadvantageous because more of the phosphate treatment liquid will cling to the treated material and be taken out.

Also, the higher the treatment liquid temperature, the greater the phosphate film amount tends to be, but a range of room temperature to 80 °C is preferred. A phosphate

film will be produced even at temperatures over 80 °C, but this is undesirable because of the higher cost of the energy needed for heating and because of higher water evaporation costs. The higher the current density, the greater is the amount of adhered film possibly obtained in a given treatment time, and a current density of at least 20 amps per square decimeter of surface treated, this unit of current density being hereinafter usually abbreviated as "A/dm²", is preferred. A phosphate film can be formed even at less than 20 A/dm², but it will take a long time to form a chemical conversion film of 6 to 20 g/m², so that productivity will be low. 100 A/dm² or less is adequate, however, and no particular benefit will be accrued by raising the current density any higher, while energy costs will be increased. At any given current density, the longer the treatment duration, the larger the possible amount of phosphate film.

Normally, the most preferred method for controlling the amount of phosphate film is by controlling the current density and time of electrolysis. Controlling the concentration, temperature, and treatment duration is possible with conventional chemical conversion treatment methods, but it is difficult to set these according to the treated material on an actual production line. The lubricative film formation method of the present invention, however, allows the specified phosphate film amount to be achieved merely by varying the setting of the current density in the cathodic electrolysis treatment, and the preferred amount of phosphate coating can be obtained within a few seconds of electrolysis at the preferred values of current density specified above.

After the phosphate treatment, the treated material preferably is rinsed with water to remove any phosphate treatment liquid that may be adhering. With the present invention, a phosphate film is formed, and then a lubricative film is formed. (This makes it possible to form a good lubricative film even on metal substrates with which this was impossible with conventional chemical conversion treatment methods involving no electrolysis. Specifically, it is possible to form a reaction type soap film after phosphate treatment on the surface of titanium or stainless steel, on which the production of a phosphate film used to be impossible, and this allows a large amount of deformation to be obtained in a single pass.) The lubrication treatment is formed by applying either a water- or oil-based lubricant-containing liquid to the outer surface of the phosphate film. The lubrication liquid is normally prepared in a treatment tank, and either the phosphate coated substrate is dipped in this tank, or the lubricant is sprayed onto the treated material, which forms a lubricative film. However, there are no particular restrictions on the contact method.

It is preferable for any water-based lubricant used to contain either an alkali metal salt of a fatty acid, a metallic soap, or a solid lubricant.

A sodium, potassium, lithium, or other such salt of a saturated or unsaturated fatty acid can be used as the alkali metal salt of a fatty acid. An unsaturated fatty acid dimeric acid, trimeric acid, or the like having at least one double bond can also be used. The alkali metal salt of a fatty acid is made into a water-based treatment liquid with a content of 1 to 20 percent by weight (hereinafter usually abbreviated as "wt%").

Any metallic soap and solid lubricant desired can be used after being dispersed in water using a surfactant, and the specific treatment method for bringing about contact is the same as that used for the alkali metal salt of a fatty acid. A metal salt of a higher fatty acid can be used as an aqueous metallic soap. Examples of higher fatty acids include lauric acid, myristic acid, palmitic acid, stearic acid, and behenic acid, while examples of metals include calcium, aluminum, magnesium, barium, zinc, and lead, etc. Of these, calcium stearate can be used to best advantage. The solid lubricant can be molybdenum disulfide, graphite, tungsten disulfide, fluorinated graphite, boron nitride, talc, mica, or PTFE (polytetrafluoroethylene). Since the alkali metal salt of a fatty acid, the metallic soap, and the solid lubricant are all water-based, a mixture of these can also be used.

When a water-based lubricant is used in a process according to the invention, the liquid lubricant preferably is brought into contact at a treatment temperature of 60 to 90 °C with a metal substrate that has undergone prior phosphate treatment, and, independently, any cold working preferably is performed only after the water in the water-based lubricant has been evaporated by a suitable drying apparatus, leaving the other constituents of the water-based lubricant to constitute a lubricative film.

It is preferable for any oil-based lubricant used according to the invention to comprise, or more preferably to consist essentially of, at least one type of component selected from among mineral oils, animal and vegetable oils, and synthetic ester oils. Machine oil, turbine oil, or spindle oil can be used as a mineral oil, while palm oil, rapeseed oil, coconut oil, castor oil, lard, beef tallow, fish oil, and the like can be used as animal and vegetable oils. A fatty acid ester of a polyhydric alcohol with a neopentyl-polyol ester structure can be used, for example, as a synthetic ester oil. A chlorine-, sulfur-, or phosphorus-based extreme-pressure additive may be added to these oil-based lubricants.

The lubricative film formation method of the present invention can be applied to a batch process in which the treated material is successively treated in the order of the separate process operations, or a continuous process, such as an in-line process in which a wire is drawn out and continuously treated. Batch processes include barrel treatment processes, which are generally performed for the treatment of forged parts.

The underlying metal substrate on which a lubricative film is formed by the method of the present invention may be subjected directly as it is to cold working, but it may also be cold worked after undergoing cold drawing at a cross sectional reduction of 15 % or less.

EXAMPLES AND COMPARISON EXAMPLES

METAL SUBSTRATES USED

Substrates of carbon steel (Type S45C), austenitic stainless steel (Type SUS 304), and aluminum (Type A6061), each with a diameter of 30 millimeters (hereinafter usually abbreviated as "mm"), were cut into pieces having a diameter of 30 mm and a height of one of each 2 mm increment from 18 to 40 mm. These were subjected to an electrolysis treatment and lubrication treatment by the procedures set forth below, after which performance tests were conducted.

PROCESS OPERATIONS — VARIATION 1:

(1) Degreasing: This consisted of a 10-minute dipping treatment at 60 °C in a 2 % solution of FINECLEANER® 4360, an alkali-based degreaser concentrate made by Nihon Parkerizing.

(2) Water rinsing: The material was immersed in room-temperature tap water, then sprayed clean.

(3) Acid pickling: The material was immersed for 10 minutes in 10 % hydrochloric acid solution in water (for carbon steel), immersed for 10 minutes in 7 % nitric acid and 3 % hydrofluoric acid solution in water (for stainless steel), or immersed for 30 seconds in 10 % nitric acid solution in water (for aluminum).

(4) Water rinsing: The material was immersed in room-temperature tap water, then sprayed clean.

(5) Surface preparation: The surface was immersed for 1 minute at room temperature in a 3 % solution of PREPALENE® Z, a colloidal titanium-based surface preparation agent concentrate made by Nihon Parkerizing, or in a 0.3 % solution of PL-X™, a metal phosphate-based surface preparation agent concentrate made by Nihon Parkerizing. (The particular treatment used is specified in one or more tables below.)

(6) Electrolysis treatment: A treatment was conducted with the treatment liquid compositions and under the electrolysis conditions given in the tables below.

(7) Water rinsing: The material was immersed in room-temperature tap water, then sprayed clean.

(8) Lubrication treatment: A lubrication treatment was conducted as described in the tables below. PALUBE® 234 and 235 (reaction type soap lubricants), PALUBE® 4612 (a non-reaction type soap), and PALUBE® 4649C (a molybdenum disulfide-based lubri-

cant), all made by Nihon Parkerizing, were used. A commercial palm oil product was used when that lubricant is shown in the tables.

PROCESS OPERATIONS — VARIATION 2

(1) Descaling: This consisted of 30 seconds of shot blasting.

5 (2) Water rinsing: The substrate was immersed in room-temperature tap water, then sprayed clean.

(3) Film treatment: A treatment was conducted with the treatment liquid composition and under the conditions given in later tables. In the comparative examples, PALBOND® 181X (a zinc phosphate-based chemical conversion treatment agent) and
10 FERRBOND® A (an oxalate-based chemical conversion treatment agent), both made by Nihon Parkerizing, were used.

(4) Water rinsing: The material was immersed in room-temperature tap water, then sprayed clean.

(5) Lubrication treatment: A lubrication treatment was conducted as shown in tables
15 below. PALUBE® 234 (a reaction type soap lubricant), PALUBE® 4612 (a non-reaction type soap), and PALUBE® 4649C (a molybdenum disulfide-based lubricant), all made by Nihon Parkerizing, were used.

PERFORMANCE TESTS

(1) Measurement of the Amount of Lubricative Film Formation

20 W1 = Film mass in g/m^2 for the lubricated material.

W2 = Film mass in g/m^2 after the lubricated material was immersed for 30 minutes in 90 to 95 °C distilled water, then dried in an oven, after which it was immersed for 30 minutes in a mixed solvent (isopropyl alcohol, n-butane, and ethyl Cellosolve™, mixed in a volumetric ratio of 6:3:1, respectively) that had been heated to 75 °C,
25 then cooled to normal temperature.

W3 = Film mass in g/m^2 after the material treated as defined for W2 was immersed for 15 minutes in an 80 °C, 5 % solution in water of CrO_3 , then rinsed with water, dried, and cooled.

30 The film amount and the lubrication amount were calculated from these measured values using the following equations:

$$\text{Film amount} = (W2 - W3)$$

$$\text{Lubrication amount} = (W1 - W2),$$

except that when the lubrication was performed with palm oil, the lubrication amount was calculated from the increase in weight before and after the oil was applied.

35 (2) Lubrication Performance

The lubrication performance was checked by means of a backward punching test

as illustrated in the drawing figures. In the backward punch test procedure, the dies **2** in Figure 1 were set to bind the circumference of the cylindrical test specimens **1** as illustrated in Figure 1, and the specimen was then subjected to a downward stroke from a punch **3** also shown in Figure 1. The punch had a diameter designed to give a 50 % cross section reduction of the test specimens **1** and to produce a cup-like molding as shown in Figures 3a through 3b. The lower dead point of the press was adjusted to give a 10 mm residual margin at the bottom of the test specimen. In this test, different test specimens with a diameter of 30 mm and a height of 18 to 40 mm in 2 mm increments were placed in the die **2**, starting with the shortest test specimen. Each test specimen tested was punched from above with a punch corresponding to a cross sectional reduction of 50 %, which formed a cup-shaped piece. The punch left 10 mm at the bottom of the test piece, and the conditions were such that the taller the test piece, the greater was the working. The inner surface of the cup was observed after this working, and the test was concluded at the point when scratches were noted. The maximum depth of the hole at which no scratches occurred was termed the good punching depth.

(3) Check for Sludge Generation

After treatment, the material was visually checked to see whether any sludge had been generated.

DETAILS OF SPECIFIC EXAMPLES AND COMPARISON EXAMPLES

Table 1 shows the concentrations of important constituents in electrolyte solutions from which a phosphate conversion coating was deposited in at least one comparison example or example according to the invention.

Table 1

Identifier for Electro- lyte in Later Tables	Concentration in Grams per Liter in the Electrolyte of:					
	Zn^{+2}	Ca^{+2}	Al^{+3}	Mg^{+2}	PO_4^{-3}	NO_3^{-}
ES1	22	None	None	None	28	31
ES2	33	None	None	None	40	46
ES3	45	None	None	None	54	62
ES4	22	6	None	None	28	50
ES5	33	None	1	None	40	51
ES6	33	None	None	1	40	51
ES7	0.15	None	None	None	0.23	0.31
ES8	45	None	None	None	56	62
ES9	21	25	None	None	66	72

Solutions of lubricants, primarily commercial products identified by trade marks, and of some surface treatment compositions used in comparison examples and their short identifiers used in later tables are listed in Table 2.

Further details of the specific examples and comparison examples and of the evaluation results of them are given in Table 3. The following conditions apply to all entries in Table 3 unless otherwise noted to the contrary in the notes thereto:

- For examples according to the invention:
 - A phosphate coating was deposited by simple direct current cathodic electrolysis at 80 °C; and
 - A conventional colloidal titanium surface conditioning pretreatment was used on the substrates after they were cleaned and before beginning the electrolysis that deposited the phosphate coating.

Table 2

Description	Identifier
Solution of 70 g/l in water of PALUBE® 235 Concentrate	L1
Solution of 200 g/l in water of PALUBE® 4612 Concentrate	L2
Palm oil	L3
Solution of 700 g/l in water of PALUBE 4649C Concentrate	L4
Solution of 100 g/l in water of PALUBE® 234 Concentrate	L5
Solution of 100 g/l in water of PALUBE® 4612 Concentrate	L6
Solution of 850 g/l in water of PALUBE 4649C Concentrate	L7
Solution of 300 g/l in water of PALUBE® 4612 Concentrate	L8
Solution of 90 g/l in water of PALBOND® 181X Concentrate	P1
Solution in water of 35 g/l of FERRBOND® A # 1 and 17 g/l of FERRBOND® A #2 Concentrates	P2
Solution in water of 30 g/l of ALBOND® A Concentrate	P3
Solution in water of 400 g/l of PALBOND® 187A Concentrate	P4

- For comparison examples:
 - When there was no electrolysis (as indicated by the word "none" in the current density column of Table 3), the chemical phosphating was performed at 80 °C; and

-- No surface conditioning pretreatment was used between cleaning the substrates and forming the phosphate coating on them.

Also, the following abbreviations are used in Table 3:

- "E" preceding an integer means "Example " according to the invention;
- 10 - "CE" preceding an integer means "Comparison Example "; and
- In the column headed "Time", "min" means "minutes" and "sec" means "seconds".

The results in Table 3 indicate that only the examples according to the invention were effective in accomplishing all of the objects of the invention. In Comparison Ex-
15 amples 1 through 7, 9, and 11 - 14, substantial amounts of sludge were formed during the phosphating operation. In Comparison Examples 7, 8, 10, 15, and 16, poor to very poor punching depth was obtainable with the lubricated film formed.

BENEFIT OF THE INVENTION

20 With the present invention, it is possible to form a thick chemical conversion film of a phosphate without generating sludge. A thick chemical conversion film can also be formed at a high level of productivity. Furthermore, a thick chemical conversion film of

Table 3

Ex- amp- le or Com- pari- son Num- ber	Process Conditions							Evaluation Results			
	Sub- strate Identi- fier	Phos- phat- ing Li- quid Iden- tifier	Phosphating Conditions		Lubrication Conditions			Coating Weights, g/m ² , for:		Good Punch- ing Depth, Milli- meters	Sludge Forme d?
			A/dm ²	Time	Lu bri- cant	°C	Minutes Expos- ure	Phos- phate Coatin g	Lubri- cant		
E1	S45C	ES1	20	10 sec	L1	80	5	11.6	5.3	48	No
E2	S45C	ES2	25	5 sec	L1	80	5	10.5	4.9	48	No
E3	S45C	ES3	35	3 sec	L1	80	5	9.9	5.1	48	No
E4	S45C	ES1	20	10 sec	L2	80	5	13.4	2.3	44	No
E5	S45C	ES2	25	5 sec	L2	60	5	12.1	2.2	44	No
E6	S45C	ES3	35	3 sec	L2	60	5	12.3	2.6	44	No
E7	S45C	ES1	20	10 sec	L2	60	0.5	13.8	5.7	44	No
E8	S45C	ES2	25	5 sec	L3	40	0.5	12.9	5.4	44	No
E9	S45C	ES3	35	3 sec	L3	40	0.5	13.6	5.8	44	No
E10	S45C	ES1	20	20 sec	L3	80	5	7.4	5.4	44	No
E11	S45C	ES4	20	10 sec	L1	80	5	7.7	4.2	52	No

... This table is continued on the next page. ...

Ex- amp- le or Com- pari- son Num- ber	Process Conditions							Evaluation Results			
	Sub- strate Identi- fier	Phos- phat- ing Li- quid Iden- tifier	Phosphating Conditions		Lubrication Conditions			Coating Weights, g/m ² , for:		Good Punch- ing Depth, Milli- meters	Sludge Forme d?
			A/dm ²	Time	Lu bri- cant	°C	Minutes Expos- ure	Phos- phate Coatin g	Lubri- cant		
E12	A6061	ES2	25	5 sec	L1	80	5	8.3	5.6	48	No
E13	A6061	ES5	25	5 sec	L1	60	5	9.6	5.2	52	No
E14	SUS304	ES6	25	5 sec	L2	30	5	8.3	2.4	48	No
E15	SUS304	ES2	25	5 sec	L4	80	3	9.7	17.4	36	No
E16	SUS304	ES2	25	5 sec	L1	80	5	8.6	6.8	32	No
E17	SUS304	ES3	80	3 sec	L4	80	3	10.2	18.0	36	No
E18	S45C	ES8	35	5 sec	L5	80	10	14.3	3.8	48	No
E19	S45C	ES8	85	2 sec	L5	80	10	10.5	2.1	48	No
E20	S45C	ES8	35	5 sec	L6	60	3	16.9	3.6	44	No
E21	S45C	ES8	85	2 sec	L6	60	3	11.3	3.7	44	No
E22	S45C	ES8	35	5 sec	L5	80	10	9.2	3.0	44	No
E23	S45C	ES8	35	5 sec	L5	80	10	8.4	3.2	52	No
E24	SUS304	ES8	35	5 sec	L7	80	10	10.8	9.8	36	No
E25	SUS304	ES9	35	5 sec	L7	80	10	9.8	10.1	36	No
E26	SUS304	ES8	35	5 sec	L7	80	10	12.3	10.4	36	No
CE1	S45C	P1	None	10 min	L1	80	5	5.3	5.5	44	Yes
CE2	S45C	P1	None	10 min	L2	30	1	6.2	3.5	40	Yes
CE3	S45C	P1	None	10 min	L3	40	0.5	6.5	2.7	32	Yes
CE4	S45C	P1	None	10 min	L1	80	5	1.3	1.5	32	Yes
CE5	S45C	ES7	10	30 sec	L1	80	5	4.5	1.6	32	Yes
CE6	S45C	ES7	10	45 sec	L1	80	5	5.6	1.9	36	Yes
CE7	SUS304	P2	None	10 min	L4	80	3	11.0	17.2	16	Yes
CE8	SUS304	P1	None	10 min	L4	80	3	0.3	10.2	0	No
CE9	A6061	P3	None	1 min	L1	80	3	10.2	4.4	52	Yes
CE10	A6061	P1	None	10 min	L1	80	3	0.2	0.1	16	No
CE11	S45C	P4	None	5 sec	L5	80	0.17	5.3	3.5	44	Yes
CE12	S45C	P4	None	5 sec	L8	60	0.17	6.2	2.2	40	Yes
CE13	S45C	P4	None	5 sec	L5	80	0.17	4.5	2.7	32	Yes
CE14	S45C	P4	None	5 sec	L5	80	0.17	3.3	2.5	32	Yes
CE15	SUS304	P2	None	5 sec	L7	80	0.17	0.9	2.7	16	Yes
CE16	SUS304	P4	None	5 sec	L7	80	0.17	0.2	0.3	0	No

Exception Notes for Table 3

- E10: The electrolysis was pulsed rather than simple direct current.
- E22: The electrolysis was at 40 °C instead of 80 °C.
- E23: The surface conditioning treatment was the dispersed solid phosphate type rather than the conventional titanium type, and the electrolysis was at 40 °C instead of 80 °C.
- E26: The surface conditioning treatment was the dispersed solid phosphate type rather than the conventional titanium type.
- CE4: The chemical conversion treatment was at 40 °C instead of 80 °C.
- CE5: Electrolysis of the substrate was anodic rather than cathodic.
- CE6: Electrolysis of the substrate was anodic rather than cathodic and was pulsed rather than simple DC.
- CE7: The chemical conversion treatment was at 95 °C instead of 80 °C.
- CE9: The chemical conversion treatment was at 90 °C instead of 80 °C.
- CE11 through CE14: The chemical conversion treatment was at 85 °C instead of 80 °C.
- CE13: A conventional colloidal titanium surface conditioning treatment was used on the substrates between cleaning and phosphating.
- CE14: A dispersed solid phosphate particle type surface conditioning treatment was used on the substrates between cleaning and phosphating.
- CE15: The chemical conversion treatment was at 95 °C instead of 80 °C.
- CE16: The chemical conversion treatment was at 85 °C instead of 80 °C.
-

a phosphate can be formed even on materials other than carbon steel, namely, stainless steel or non-ferrous materials. If the thick chemical conversion film of a phosphate formed by the method of the present invention is coated with a conventional water- or oil-based lubricant, an excellent lubricative film for cold working can be obtained.

CLAIMS

1. A process for forming a lubricative film for cold working on a metal substrate, said process comprising the following operations:

(I) bringing said metal substrate into contact with an aqueous electrolyte solution comprising water and:

(A) dissolved zinc cations;

(B) dissolved phosphate anions; and

(C) at least one dissolved auxiliary acid other than phosphoric acid, said auxiliary acid having at least a first ionization constant that is greater than the third ionization constant for phosphoric acid; and, optionally, other constituents as detailed further below,

this aqueous electrolyte also being in contact with a counter-electrode that is not said metal substrate to be cold worked, so that an electric current can pass through the counter-electrode as anode, the aqueous electrolyte solution by ionic conduction, and said metal substrate as cathode;

(II) passing through said metal substrate while it remains in contact with said aqueous electrolyte solution an electric current that has a net cathodizing character at said metal substrate for a sufficient time to form an adherent solid phosphate conversion coating over said metal substrate;

(III) discontinuing contact between said aqueous electrolyte solution and said metal substrate bearing said adherent solid phosphate conversion coating; and

(IV) applying to the exterior surface of said solid phosphate conversion coating, when it is not in contact with said aqueous electrolyte solution, a water- or oil-based lubricant coating.

2. A process according to claim 1, wherein said aqueous electrolyte solution in operation (I):

- comprises at least 20 g/l of dissolved zinc cations and at least 20 g/l of dissolved phosphate anions; and

- has a pH value at least as low as the pH value of a hypothetical reference electrolyte solution that contains the same actual amounts of dissolved zinc and phosphate ions as does said aqueous electrolyte solution and in addition contains at least 30 g/l of nitric acid as its only auxiliary acid.

3. A process according to claim 2, wherein said aqueous electrolyte solution additionally comprises at least one type of divalent or trivalent metal ions selected from the group consisting of magnesium, aluminum, calcium, manganese, chromium, iron, nickel,

and copper.

4. A process according to claim 3, wherein said aqueous electrolyte solution comprises a concentration of calcium ions such that the molar ratio of calcium ions to zinc ions is from 0.1:1 to 2:1.

5 5. A process according to claim 4, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

6. A process according to claim 5, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter
10 of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

7. A process according to claim 6, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed
15 metallic soaps, and dispersed solid lubricants.

8. A process according to claim 6, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

9. A process according to claim 1, wherein said aqueous electrolyte solution additionally comprises at least one type of divalent or trivalent metal ions selected from the
20 group consisting of magnesium, aluminum, calcium, manganese, chromium, iron, nickel, and copper.

10. A process according to claim 9, wherein said aqueous electrolyte solution comprises a concentration of calcium ions such that the molar ratio of calcium ions to zinc ions is from 0.1:1 to 2:1.
25

11. A process according to claim 10, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

12. A process according to claim 11, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter
30 of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

13. A process according to claim 12, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant

substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

14. A process according to claim 12, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

15. A process according to claim 1, wherein before operation (I), said substrate is acid pickled and then rinsed with water.

16. A process according to claim 15, wherein after being acid pickled and rinsed with water, said substrate is brought into contact with a surface conditioning liquid containing colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

17. A process according to claim 16, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

18. A process according to claim 16, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

19. A process according to claim 1, wherein before operation (I), said substrate is brought into contact with a surface conditioning liquid comprising colloidal titanium, dispersed metal phosphate particles including particles with a diameter of 5 μm or less, or both colloidal titanium and dispersed metal phosphate particles with a diameter of 5 μm or less.

20. A process according to claim 19, wherein the lubricant coating applied in operation (IV) is a water-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of dissolved alkali metal salts of fatty acids, dispersed metallic soaps, and dispersed solid lubricants.

21. A process according to claim 19, wherein the lubricant coating applied in operation (IV) is an oil-based lubricant that comprises at least one type of lubricant substance selected from the group consisting of mineral oils, animal oils, and synthetic ester oils.

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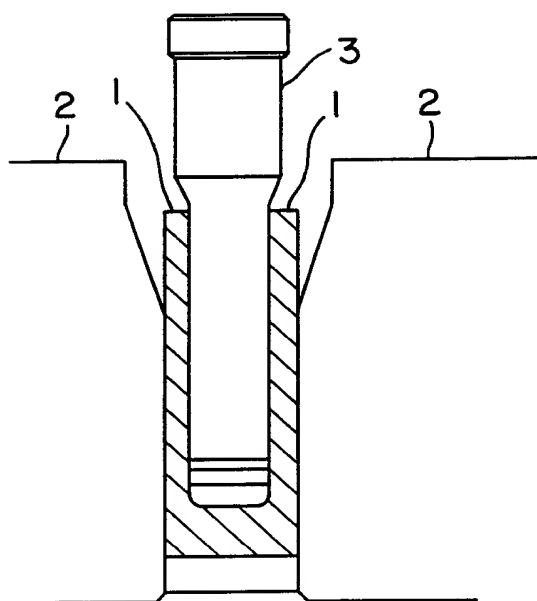


FIG. 1

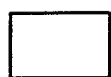


FIG. 2a

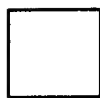


FIG. 2b



FIG. 2c



FIG. 2d



FIG. 3a



FIG. 3b

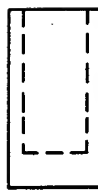


FIG. 3c

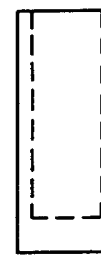


FIG. 3d

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/21117

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C25D 11/36; C23C 28/00

US CL :205/199, 318

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 205/199, 318

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
phosphate, lubricate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 4,874,480 A (SONODA et al) 17 October 1989, column 2, lines 18-34 and 56-62.	1, 3, 6-9, 12-14, 16-21 ----- 2, 4, 5, 10, 11, 15
Y	US 5,401,381 A (SEIDEL et al) 28 March 1995, column 6, line 63 to column 7, line 12.	1-21
Y	US 5,503,733 A (SPECKMANN et al) 02 April 1996, abstract.	1-21



Further documents are listed in the continuation of Box C.



See patent family annex.

* "A" "E" "L" "O" "P"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance earlier document published on or after the international filing date document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed	"T" "X" "Y" "&"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document member of the same patent family
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Date of the actual completion of the international search

19 DECEMBER 1999

Date of mailing of the international search report

01 FEB 2000

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

WILLIAM LEADER

Telephone No. (703) 308-0661